COATINGS. ENAMELS

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POLYFUNCTIONAL THIN-FILM MATERIALS BASED ON OXIDES

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Thin films based on oxides of *p*- and *d*-elements are obtained by precipitation from film-forming solutions. Composites are developed based on oxides of group IV of the periodic system, yttrium and iron triad elements. By varying the component ratio, one can control the optical properties of films used as coatings for protection against from the effect of UV radiation, selectively absorbing the visible spectrum range, and as sun-shielding color-correcting coatings.

Deposition of thin film materials on the surface of light-source bulbs and window panes makes it possible to solve various problems of redistribution of electromagnetic radiation intensity in certain spectra ranges [1]. With respect to the functional purpose, it is possible to distinguish interference coatings and UV filters selectively absorbing the visible spectrum range. The criteria for application of such coatings are sufficiently diverse. They primarily include simplicity of production technology, high thermal stability, resistance to radiation, chemical resistance, and an acceptable level of adhesion. The above requirements can be met by thin films based on oxides of some *p*- and *d*-elements of group IV of the periodic system of elements (SiO_2, TiO_2, and ZrO_2). Introduction of yttrium, iron, cobalt, and nickel oxides in certain ratios into such films makes it possible to obtain thin-film coatings with a required set of physicochemical properties.

Thin film coatings were synthesized using film-forming solutions (FFS) based on tetraethoxysilane $Si(C_2H_5O)_4$, tetraethoxytitanium $Ti(C_2H_5O)_4$, zirconium oxochloride $ZrOCl_2 \cdot 8H_2O$, yttrium, iron, cobalt, and nickel salts (chlorides, nitrates), and also ethyl alcohol. The total concentration of salts converted to oxides was 0.4 M, and the molar content of yttrium and iron triad element oxides varied from 0 to 100%. Films were obtained on glass and quartz substrates using the method of centrifuging (rotational speed of the substrate being 3000 min^{-1}) and drawing from solutions (drawing velocity of 5 mm/sec) at a temperature of 290 – 300 K. Heat treatment was carried out in two stages at temperatures of 330 and 770 – 870 K. The processes occurring in FFS and in the formation of films were studied using viscosimetry (an Ostwald viscosimeter), differential thermal analysis (Q-1500 Paulik – Paulik – Erdey system), and x-ray phase (DRON-3) analysis. The optical characteristics of films were studied on an LÉF-3M laser ellipsometer and an SF-20 spectrophotometer, and the microstructure of the films obtained was studied on an MII-4 microinterferometer.

The possibility of obtaining thin film materials depends on the film-forming capacity of initial compounds, their concentration, and the conditions of film synthesis: air temperature and moisture, the rate of deposition of solution, heat treatment temperature conditions. The film-forming capacity of solutions based on alkoxy-compounds and oxo-salts of group IV elements depends on the capacity of the initial substances to enter in reactions of hydrolytic polycondensation and form colloid solutions and mono- and polynuclear complex compounds. In doing so, the molar mass of emerging compounds increases and, accordingly, the viscosity of the solution changes. Viscosity variation can be used to estimate the stability of an FSS in time, which is significant for technology. Figure 1 shows the kinetic curve of viscosity variation for the FFS based on tetraethoxysilane versus storage duration.

Viscosity in storage changes in three phases. A solution matures in the first 2 days, and the viscosity of the system sharply increases at that time as a consequence of hydrolysis and polycondensation of OH-groups, which results in the formation of polysiloxane [2, 3]. In the next 43 days the solution viscosity is stabilized to some extent, the processes in the FFS slow down, and the reactions of hydrolysis and polycondensation proceed at an insignificant rate due to spatial complications. After 45 days the solution starts aging, and its viscosity sharply increases due to cyclization of siloxanes. The solution after some time transforms into gel.

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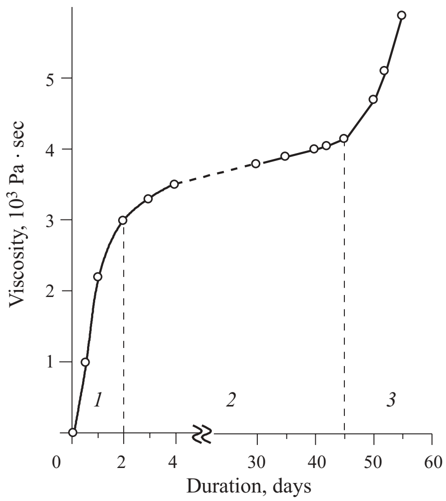

Fig. 1. Viscosity of FFS based on tetraethoxysilane depending on storage duration: *1*, *2*, and *3*) duration of maturing, suitability, and aging of FFS, respectively.

Films obtained from such solutions are nonuniform and often flake, which makes them unfit.

Thus, the conditions of film production are limited by the ranges of maturing and aging of FFS, and the solution viscosity should be within the limits between 3×10^{-3} and 4.5×10^{-3} Pa · sec. Such asolution is suitable for producing films for 43 days after 2 days of maturing (Table 1). The hydrolysis and polycondensation reactions in the FFS based on tetraethoxytitanium proceed at a higher rate, as a result of which maturing occurs within a very short time. These solutions remain suitable for film production during 6 days. Reactions of hydrolysis in alcohol solutions of zirconium oxochloride are rather intense; the acidity of forming solutions is significantly higher than the acidity of solutions based on tetraethoxysilane (TEOS) and tetraethoxytitanium. Accumulation of protons facilitates a redox equilibrium shift and slows down further process of hydrolysis. Therefore, the time of serviceability of FFS based on zirconium oxychloride is significantly longer.

TABLE 1

Composition of films prepared from FFS, %	Duration, days		
	FFS maturing	suitability of FFS for film production	FFS aging
$700SiO_2$	2	43	6
$100TiO_2$	0.5	6	2
$100ZrO_2$	3	300	60
$90SiO_2 - 10TiO_2$	1	30	2
$90SiO_2 - 10ZrO_2$	1	22	2
$90SiO_2 - 10Y_2O_3$	2	53	6
$90ZrO_2 - 10Fe_2O_3$	6	12	180
$90ZrO_2 - 10CoO$	4	300	60
$90ZrO_2 - 10NiO$	4	150	180
$90ZrO_2 - 10Y_2O_3$	8	300	180

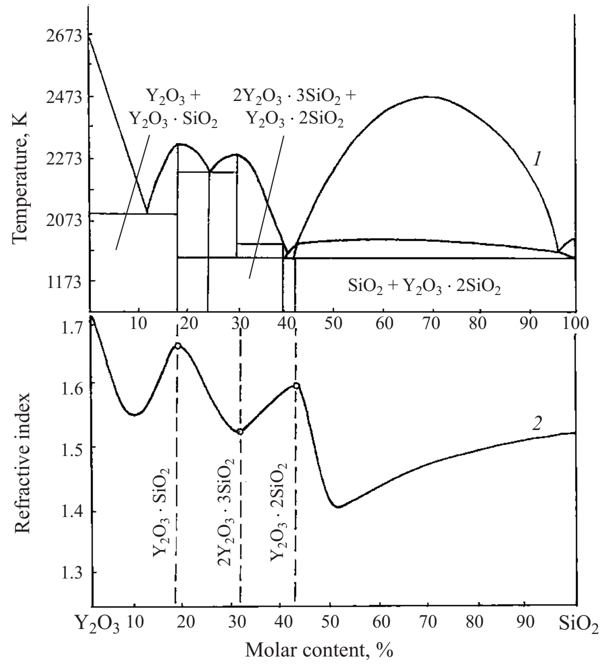

Fig. 2. Phase diagrams of the system $SiO_2 - Y_2O_3$ (*1*) and composition – refractive index of films (*2*).

The production of binary oxide films depends on compatibility of several oxide-forming salts (mutual hydrolysis or solubility). Yttrium, cobalt, and nickel chlorides and nitrates, which do not have film-forming properties in alcohol solutions, have an effect on the structure of colloid particles and under certain concentrations decrease or increase the stability of FFS. Thus, introduction of yttrium nitrates into a TEOS-based FFS at the initial stage intensifies the processes of hydrolysis and condensation of TEOS in the solution, then the processes in the FFS slow down, the FFS becomes stabilized, and the interval of serviceability for film production grows from 43 to 53 days. Polycondensation of TEOS can be accelerated by introducing yttrium salt, due to the formation of an intermediate complex.

As the acceptor compounds $Y(NO_3)_3$ dissolves in the donor solvent C_2H_5OH, solvate complexes of different compositions may be formed due to the high coordination number of Y^{3+} and its capacity to form complex compounds. Later on, after cyclic polysiloxane macromolecules are formed in the system, macromolecule associates (micelles) may arise. Micelle formation in non-aqueous media, as a rule, is the result of attraction forces between the polar polymer groups and reactions between the radical and the solvent. The forces of interaction between molecules in micelles are mainly due to dipole-dipole interaction and possible hydrogen bonds. The electrostatic stability factor is typical of most colloid systems. Stabilization depends significantly on the force of fixation of the molecules.

In developing interference filters it is often impossible to select an individual oxide with a required refractive index. In such case the use of binary oxide films is very convenient,

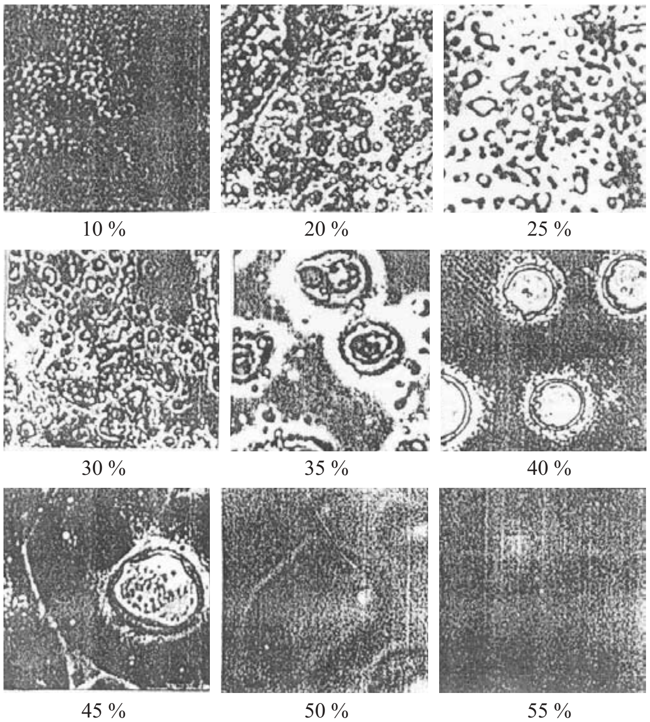

Fig. 3. Microstructure of films of $SiO_2 – Y_2O_3$ system in stratification ranges with varying content of Y_2O_3.

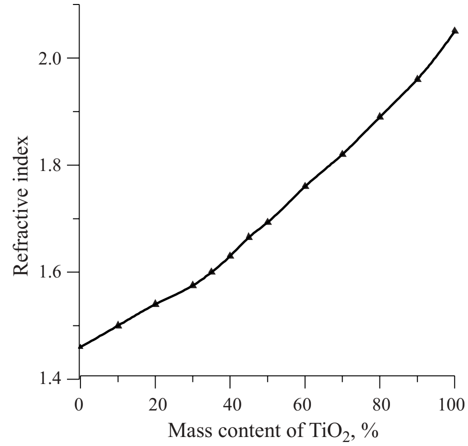

Fig. 4. Refractive index of films of system $SiO_2 – TiO_2$.

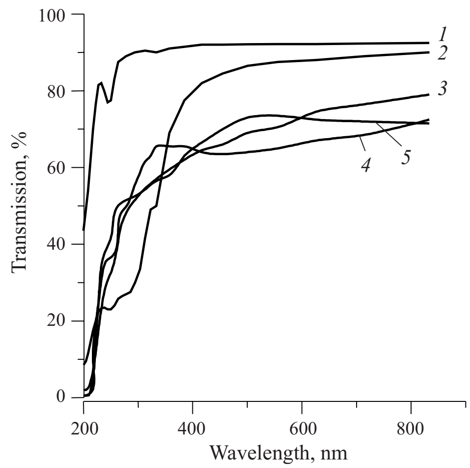

Fig. 5. Transmission spectra of films in the system $ZrO_2 – NiO$ on quartz substrates: *1*) quartz substrate; *2*, *3*, *4*, and *5*) films obtained on quartz substrates from FFS with molar content of nickel nitrate 80, 20, 10, and 0%, respectively.

since the refractive index of film will depend on the refractive indexes of the components and their ratio. An equilibrium phase diagram of an oxide system is significant for the selection of a composition for multicomponent oxide films. Film properties within the range of existence of a mixture of oxides change linearly, the formation of solid solutions leads to a deviation from the linear dependence, and formation of chemical compounds correlates with emergence of extremums on the composition – property diagram. Thus, the composition – refractive index diagram for films of the $SiO_2 – Y_2O_3$ system exhibits extrema correlating with the formation of yttrium silicates (Fig. 2).

The microstructure of these films was investigated using electron-diffraction and microscopic methods (Fig. 3). With a low Y_2O_3 content (up to 5%, here and elsewhere mol.% unless otherwise specified), the films are close-grained, which is typical of SiO_2. As the content of Y_2O_3 grows from 5% to 55%, stratification is observed in the system and films are either formed with inclusions of a second phase, or (with 50 – 55% Y_2O_3) are laminar. With Y_2O_3 content ranging from 55 to 85%, the film macrostructure is fine-grained, correlating with SiO_2 having inclusions of coarse-grained silicate structure. With a Y_2O_3 content over 85%, the film macrostructure is close to the crystalline structure of this oxide.

However, it should be taken into account that film material exists in a nonequilibrium metastable state, and data of the equilibrium phase diagram of an oxide system do not always coincide with the composition – property diagrams for the film. In interpreting the composition – property diagram, one should also take into account the possibility of formation of an amorphous polymer-like structure in films, which is especially typical of films on glass substrates. Thus, the refractive index of films of the $ZrO_2 – SiO_2$ and $TiO_2 – SiO_2$ systems on glass substrates depend nearly linearly on the ratio of the components, which does not agree with data on the equilibrium phase diagram of the oxide system (Fig. 4).

Thin film coatings based on oxides of *d*-metals have an intense fundamental absorption band; the absorption edge wavelength λ_{ed} is located in the UV spectrum range, for instance for ZrO_2 $\lambda_{ed} \approx 220$ nm, and for TiO_2 $\lambda_{ed} \approx 300$ nm, which makes it possible to use them in UV filters. The molar extinction coefficient in this range is within the limits of $10^3 – 10^4$ mole$^{-1} \cdot$ cm^{-1}. Introduction of oxides into coatings based on ZrO_2 and TiO_2 makes it possible to shift the fundamental absorption edge to one side or another [5].

Thus, introduction of silicon oxide into films based on ZrO_2 and TiO_2 shifts λ_{ed} toward lower values, for instance, $SiO_2 – TiO_2$ to a range of 220 – 300 nm, and $SiO_2 – ZrO_2$ to a range of 180 – 220 nm. An increase in a TiO_2 content displaces λ_{ed} to the long-wave range, from 220 to 290 nm. Introduction of iron, cobalt, and nickel oxides intensifies absorption not only of ultraviolet but of visible radiation as well. By varying the ratio between zirconium oxide and iron triad oxides, it is possible to vary within a wide range the transmission coefficient in the visible spectrum range and the absorption edge from 200 to 800 nm (Fig. 5). This makes it possible to control radiation intensity in the visible spectrum range, to obtain coatings with a sun-shielding effect, and to correct the spectral composition of light sources in the ultraviolet and visible spectrum ranges.

Thus, polyfunctional thin film composites have been obtained on the basis of oxides of some *p*- and *d*-elements of group IV of the periodic system. Introduction of yttrium, iron, cobalt, and nickel oxides into the composition of these films makes it possible to synthesize thin film coatings with the required set of optical properties. These films can be used in coatings protecting from UV radiation, selectively absorbing the visible spectrum range, and in sun-shielding color-correcting coatings.

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